## PATENT SPECIFICATION

**1264 196** (11)

## NO DRAWINGS

(21) Application No. 34850/69 (22) Filed 10 July 1969

(31) Convention Application No. 743641 (32) Filed 10 July 1968 in

(33) United States of America (US)

(45) Complete Specification published 16 Feb. 1972

(51) International Classification B 32 b 25/08 B 29 d 9/00

(52) Index at acceptance

B5N 17X 17Y 221 22X 252Y 254Y 266Y 270Y 277Y 280Y 284Y 285Y 286Y 298Y 322Y 324Y 326Y 327 328 332Y 333Y 334Y 335Y 54X 560 669 750 769 796

B2E 209 23Y 323 335 336 337 339 346 347 34Y 355 357 35Y 368 435 436 43Y 44Y 467 475 476 48Y 492 49Y 508 510 520 535 536 54Y 552 555 556 557 55X 55Y 566 56Y 599 59X 59Y 620 626 62X 62Y 638 649 65Y 668 718 743 755 756 757 766 767 76Y 775 777 77Y

B5B 230 250 25Y 35Y 363 368 369 412 422

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## (54) LAMINAR BLASTOMERIC FILM STRUCTURES

We, E. I. Du Pont de Nemours (71)AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, located 5 at Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly des-10 cribed in and by the following statement: --

This invention relates to a laminar film structure.

Extensible transparent film is widely used for packaging, and particularly for wrapping 15 of foodstuffs such as meat. To be used in currently available peckaging machinery, howevery, such film must have a relatively low coefficient of friction. Generally, those transparent films having relatively high elastomeric properties are characterized by poor surface slip or tacky surfaces, while films having good surface slip tend to have relatively low extensibility. Attempts have previously been made to take advantage of the desirable qualities of two or more different films by lamination. These attempts have been unsuccessful, however, since such structures have heretofore exhibited a tendency to delaminate upon stretching, making them unsuitable for most packaging operations.

The present invention provides film structures which combine relatively high extensibility with good surface slip. Specifically, the present invention provides a laminar film structure comprising an inner layer of elastomeric polymer and two outer layers of polymeric resin, the outer layers each having an

extensibility equal to at least 50% of the extensibility of the inner layer, at least one of the outer layers having a coefficient of 40 friction to metal of less than 0.50.

The materials which are used in the manufacture of the laminated structures of the present invention must be combined with regard to their extensibility as indicated above, 45 more elastic core materials requiring more clastic materials for the outer layers. Materials which can be used for the inner layer of these structures generally are elastomers which have an extensibility of greater than 400% and include, for example, natural and synthetic rubbers such as syrene-butadiene polymers, ethylene-propylene copolymers and terpolymers; polyurethane; chlorinated rubber, reclaimed rubber; cyclized rubber; rubber hydrochloride; polyisobutylene; isobutylene isoprene copolymers; polyisoprene; polychloroprene; polybutadiene; copolymers of butadiene or isoprene with styrene or acrylonitrile; and copolymers of propylene 60 and ethylene with other unsaturated compounds such as hexene and hexadiene.

Polymeric resins which can be used in the outer layers of the laminar structure must have an extensibility of at least 50%, of the 65 particular inner layer used, that is, above about 200%. It is also preferred that the polymeric resin be heat scalable, to facilitate packaging by usual techniques. Polymeric resins which can be used in the outer layers include, for example, ethylene-vinyl acetate copolymers; ethylene copolymerized with alkyl acrylic esters having 1-5 carbon atoms in the alkyl group, e.g., methyl acrylate, ethyl



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acrylate, butyl acrylate, and butyl methacrylate; and ethylene and propylene copolymers. Especially preferred are ethylene copolymers wherein the commonmer comprises
about from 25 to 35%, by weight of the polymeric composition. The two outer layers can
be the same or different, depending on manufacturing convenience and the particular
physical properties desired in the outer layers.

At least one outer layer of the film structures of the present invention has a coefficient of friction to metal of less than 0.50. For some packaging operations, such as the wrapping of bread and meat, it is desirable to have one surface of the laminar structure exhibit a coefficient of friction to metal of greater than 0.50 and the other less than 0.50 so that one surface of the film will cling to the wrapped article and the other will have good surface slip necessary for the packaging apparatus. This coefficient of friction can be measured by techniques generally used in the art, such as that described in Owens, 8 Journal

of Applied Science 1465 (1964). The desired slip characteristics and other physical properties of the outer layer can be inherent in the polymeric resin used or the resin can be modified by the incorporation of additives generally used to tr or nonblocking, non-fogging, and slip char existics. For example, the addition of additives such as N,N'-dioctayladipamide, calcium stearate, glycerol monostearate, glyceryl distearate, crucamide, oleamide, N-oleyl palmitamide or silica to various copolymers often improves the non-blocking, non-fogging, and slip characteristics of many of the polymeric resins indicated above. These additives generally comprise less than 5% and usually about from 40 1—2% by weight of the polymeric resin.

One combination of elastomeric polymer and polymeric resin which has been found to be particularly satisfactory in the laminated structures of the present invention comprises outer layers of ethylene-vinyl acetate copolymer comprising about 28%, by weight vinyl acetate and an inner layer of styrene-butadiene rubber.

The laminated structures of the present 50 invention can be produced by any of the usual extrusion techniques depending on the compatibility of the particular melt characteristics of the components. The three-ply structure can be prepared by extrusion lamination 55 wherein the outer layers are preformed films and the clastomeric inner layer is extruded between them by a suitable melt laminating apparatus; or one of the outer layers can be preformed and the remaining layers applied 60 by extrusion, lamination, or melt coating. It is generally most economical, however, to coextrude the three-ply structure simultaneously through a three-ply extrusion die of the type generally used in the art.

The particular thickness of the individual

films of the structure is not a critical feature of the present invention. However, to obtain maximum electromeric character for the laminated structure, the inner layer should be thicker than the combined outer layers. It is preferred that the combined thicknesses of the two outer layers constitute no more than one-third of the total thickness of the three-ply structure. For example, a film structure in which the inner: outer layer thickness ratio is about 7:3 is found to give especially good elastomeric performance. The outer layers may be of the same or different thickness. However, the thickness of each outer layer should not be less than 0.15 mil.

In the following examples, which illustrate specific embodiments of the present invention, percentages are by weight unless otherwise indicated.

## EXAMPLE 1

A three-ply laminar structure is prepared by coextrusion of resins through a 3 channel, single exit slot die at a temperature of 190°C. The outer layers both are an ethylene/vinyl acetate copolymer comprising 28% vinyl acetate to which has been added 0.25% N,N'-dioctyladipamide, 2% calcium stearate and 0.6% of glycerol monostearate, to obtain non-blocking, good slip and non-logging properties. The inner layer or core is a styrene/butadiene rubber commercially available from Shell Chemical Co. as "Thermolastic (Registered Trade Mark) 125."

The inner core of the resulting film has a thickness of 1.5 mils and the outer layers are each 0.3 mil in thickness. The coefficient of friction to metal is 0.40. The extensibility of the outer layers is 50% of the inner layer, the outer layers being 500% and the inner layer being 1000%. The film operates well on an over-wrap machine for the over-wrapping of articles. A samper of the film hand wrapped around slices of red meat and heat sealed to form the closure shows excellent color retention of the packaged article.

The resistance of the film to fogging is determined as follows. A 100 mil beaker is filled to within 1/2 inch of the top with water at 120°F. A 4"×4" piece of the test film is fastened over the mouth of the beaker with a rubber band. At the end of one hour no evidence of fog or minute droplets of water on the inner film surface is observed.

The blocking performance of the film is tested by the following procedure. 15 to 20 120 sheets of 4"×4" film are piled in a stack front to back. The stack is placed between two 4"×4" sheets of chipboard and wrapped to form a package in waxed kraft paper. The package is placed on a smooth sheet of metal 125 at least 1/16 in. thick and approximately 6 in. square. A 4"×4" lead weight with a smooth face and having a weight of 25 lbs. (1.5 lb/sq. in.) is placed on the package of

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sheets, and the entire assembly is placed in an oven maintained at 55°C. for 16 hours. The package of sheets is removed from the oven and allowed to cool to room temperature. The cooled package of sheets is unwrapped, the chipboard removed, and the stack of sheets grasped by thumb and forefinger in the center of the stack. A shearing force is then applied with care taken to avoid the stack or disturbing its edge. The film is found to exhibit satisfactory blocking performance, in that the stacks readily separate into two or more groups of sheets.

EXAMPLE 2

Example 1 is repeated except that one of the two outer layer resins does not contain the additives to provide good slip, non-blocking and non-fogging performance. One surface of the resulting laminar structure shows a crefficient of friction to metal of 0.40 whereas the opposite surface shows a coefficient of friction to metal of 1.0. The resulting film is found to be well suited for wrapping of articles such as meat, bread, and various small items in that the wrapping clings effectively to the wrapped article while the opposite surface, having good surface slip, permits effective shaping and application of the film on to the article being packaged.

WHAT WE CLAIM IS:-

1. A laminar film structure comprising an inner layer of an elastomeric polymer and

two outer layers of polymeric resin, the outer layers each having an extensibility equal to at least 50% of the extensibility of the inner 35 layer, at least one of the outer layers having a coefficient of friction to metal of less than 0.50.

2. A laminar structure according to Claim 1 wherein the extensibility of the inner layer is at least 400% and the extensibility of the outer layers is at least 200%.

3. A laminar structure according to Claim 1 or Claim 2 wherein the ratio of the thickness of the inner layer to the combined outer layers is greater than 2:1.

4. A co-extruded film structure according to any one of Claims 1 to 3 wherein the inner layer comprises styrene-butadiene rubber and the outer layers comprise ethylene- ii yl acetate 50 copolymer having a vinyl acetate intent of from 25 to 35% by weight.

5. A laminar film structure having high extensibility and surface slip substantially as hereinbefore described.

6. A three-play laminar film structure substantially as hereinbefore described in Example 1 or Example 2.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Learnington Spa, 1972. Published by The Patent Office, 25-Southampton Buildings, London, WCLA 1AY, from which copies may be obtained.